THE SPEED OF SOUND AND OTHER THERMODYNAMIC QUANTITIES OF DILUTE AQUEOUS ELECTROLYTE SOLUTIONS BY AN ULTRASONIC VELOCIMETER COMPARISON TECHNIQUE

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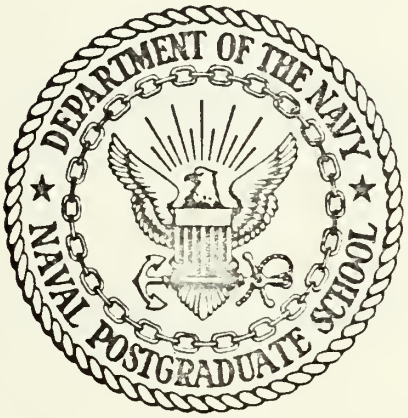

THESIS

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June 1972

The Speed of Sound and Other Thermodynamic Quantities of Dilute Aqueous Electrolyte Solutions by an Ultrasonic Velocimeter Comparison Technique

by

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ABSTRACT

A very precise velocimeter has been developed and utilized to measure changes in the speed of sound as a function of the concentration of aqueous electrolyte solutions. The experimental results indicated that the speed of sound can be measured with a precision of $\pm$ 3 cm/sec. Using 2 velocimeters for comparison, one filled with distilled water and one filled with dilute aqueous solutions of NaCl, four separate runs were conducted at concentrations of 2×10^{-1}, 4×10^{-2}, 4×10^{-3}, and 4×10^{-4} moles/liter. The ratios of superposition frequencies vs. pressure, over the pressure range of 0 to 1500 psi in increments of 500 psi, and temperature, over the temperature range of 35° to 55°C in increments of 10°C, were obtained. The change in the speed of sound as a function of the concentration of NaCl in the concentration range 2×10^{-1} to 4×10^{-4} moles/liter is in agreement with data from Garnsey, Boe, Mahoney, and Litovitz from the Journal of Chemical Physics, v. 50, n. 12, pp. 5222-5228, 15 June 1969. The slope of the line at 45°C is 56.0 (m/sec)/(mole/liter) in reasonable agreement with the slope of 66.0 (m/sec)/(mole/liter) from Litovitz et al for 25°C.

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ACKNOWLEDGEMENTS

The author would like to express his grateful appreciation to Associate Professor A. B. Coppens for his suggestions, interest, understanding and advice in the preparation of this Thesis, and to Mr. R. C. Moeller and Mr. M. K. Andrews for their assistance in construction and design of the necessary equipment.

I. INTRODUCTION

A. PURPOSE

This research was conducted to determine the speed of sound and other thermodynamic quantities of dilute aqueous solutions of NaCl by a velocimeter-comparison technique.

B. PRINCIPLE OF VELOCIMETER

The velocimeters used in this experiment were based on the pulse technique introduced by Pellam and Galt in 1946,[1] as modified by a specialized technique known as the pulse superposition method. In the pulse technique a sinusoidal pulse is applied to a crystal tansducer that is in contact with the liquid to be tested. The crystal converts the electrical pulse into an acoustical pulse which is then transmitted through the sample liquid to the second crystal where the pulse is reflected back to the first crystal. Each time the pulse returns to the second crystal, part of its energy is converted to an electrical signal, and the rest is reflected back through again. The pulse repetition rate is adjusted such that a subsequent pulse arrives at the second crystal at the same time the re-reflected previous pulse arrives. Thus the pulse repetition rate is equal to the round-trip transit time, $t = 1/f$ and using $c = 2\ell f$ where c is the speed of sound in the liquid, ℓ is the length of the velocimeter and f is the pulse repetition rate, the speed of sound may be determined.

II. EQUIPMENT

A. CRYSTALS

The crystal transducers are x-cut quartz disks each with a diameter of 1.0000 inch and a thickness of approximately 0.03 inch. The natural resonance of the crystals occurs at 5 MHz $\pm$ 1%. The plating is complete on one side and over a circle of 5/8 inch diameter on the other side. Electrodes are evaporated thin films of chrome and gold.

B. DELAY LINES

Figures 1 and 2 show the delay lines each of which consisted of an outer delay line jacket, inner sleeve, two end pieces, "O" rings (Parker compound C-557-7), stainless steel washer, and crystal transducers. The outer delay line jacket and the pressure vessels (See Pressure System) were of slightly different dimensions and were coded as follows: Outer delay line jacket A had ends coded • and •• and the end pieces were coded • and •• . Similarly outer delay line jacket B had ends coded ∴ and ⁘ and the end pieces were coded ∴ and ⁘ . The pressure vessels were coded A and B. Outer delay line jacket A was always placed into pressure vessel A and outer delay line jacket B was always placed into pressure vessel B. The inner sleeves were interchangeable between delay line jackets A and B. One modification was made to the existing delay line to correct faulty electrical contacts to the crystals of the velocimeter. The

modification consisted of redesigning the teflon insulator as shown in Figure 2 and allowing the connecting spring to pass completely through the end pieces thus providing solid electrical contact between the crystal transducers and the brass bar (See Figure 4) which was a major modification to the ends of the pressure vessel.

C. PRESSURE SYSTEM

The pressure system is shown in Figures 3-5. The pressure gauge is a Heise gauge with a range of 0-2000 psi, with a smallest scale division of 2 psi. Figure 3 shows the thermal jacket (used to correct for thermal gradients within the oven) and the two pressure vessels. The existing pressure vessels using soapstone as a sealant for the electrical connections would not contain the pressure despite a rated capacity of 20,000 psi. Pressure leaks of approximately 0.06 psi/sec at a gauge pressure of 1500 psi were a problem. A possible solution to the problem was the substitution of nylon for soapstone as the sealing material but pressure leaks of the same order of magnitude were observed when this substitution was made. However, pressure leaks were never observed (using a solution called "Snoop" to detect minute gas leaks) on the ends of the pressure vessels where each pressure vessel cap tightens down to a metal-to-metal contact compressing a large "O" ring. The absence of pressure leaks on the ends of the pressure vessels indicated that a similar design might work on the electrical connectors where the soapstone and nylon had failed. Figure 4 shows these modifications to the

pressure vessels. A brass bar, a small "O" ring, a brass nut to tighten the assembly to a metal-to-metal contact, and a nylon sleeve to provide the necessary insulation were sufficient to provide a pressure seal. Subsequent runs of the equipment demonstrated the ability of the pressure system to hold pressures of approximately 1500 psi for days with no pressure loss. A minor modification was made to the thermal jacket by removing two screws located at the top of the thermal jacket to allow pressure vessels A and B to be interchanged within the oven for calibration checks of the system. Pressure is supplied to the pressure vesself from a bottle of compressed nitrogen as shown in schematic in Figure 5. Pressure to the pressure vessels is obtained by closing valves 3, 5, and 8 and opening valves 1, 4, 6, and 7. Then valve 2 is opened very slowly (to prevent damage to the gauge) until the desired pressure is obtained as indicated on gauge B. Gauge A indicated the amount of pressure remaining in the supply bottle.

D. TEMPERATURE CONTROL SYSTEM

Temperature range of ambient to 100^{o}C with stability of $\pm$ 0.5^{o}C was provided by an Aminco Forced-Convection Oven and is shown in Figure 6. A motor-driven blower produces movement of a large volume of heated air horizontally across the workchamber after first passing it over heaters which circle the inner diffusion walls. This configuration was designed to distribute uniform heat through the entire work chamber eliminating hot and cold pockets, but difficulties

experienced by Lieutenant Dawson[2] in his prior research prompted him to determine an orientation of the thermal jacket reducing the temperature increment between the pressure vessels. Lieutenant Dawson determined the right side of the oven to be slightly warmer than the left side and to compensate for this a thermal jacket was utilized. The aluminum thermal jacket has a sliding fit with the two pressure vessels which are interchangeable within the thermal jacket.

E. TEMPERATURE MEASUREMENT

Temperature was measured using a thermistor thermometer plug-in module with a system accuracy (instrument and probe) of $\pm$ 0.45°C and a precision of $\pm$ 0.005°C[3]. Probes were placed into two holes drilled into the middle of the thermal jacket. Both probes were used throughout the experiment and probe B typically measured temperatures approximately 0.05°C higher than probe A in the temperature range 35° to 55°C.

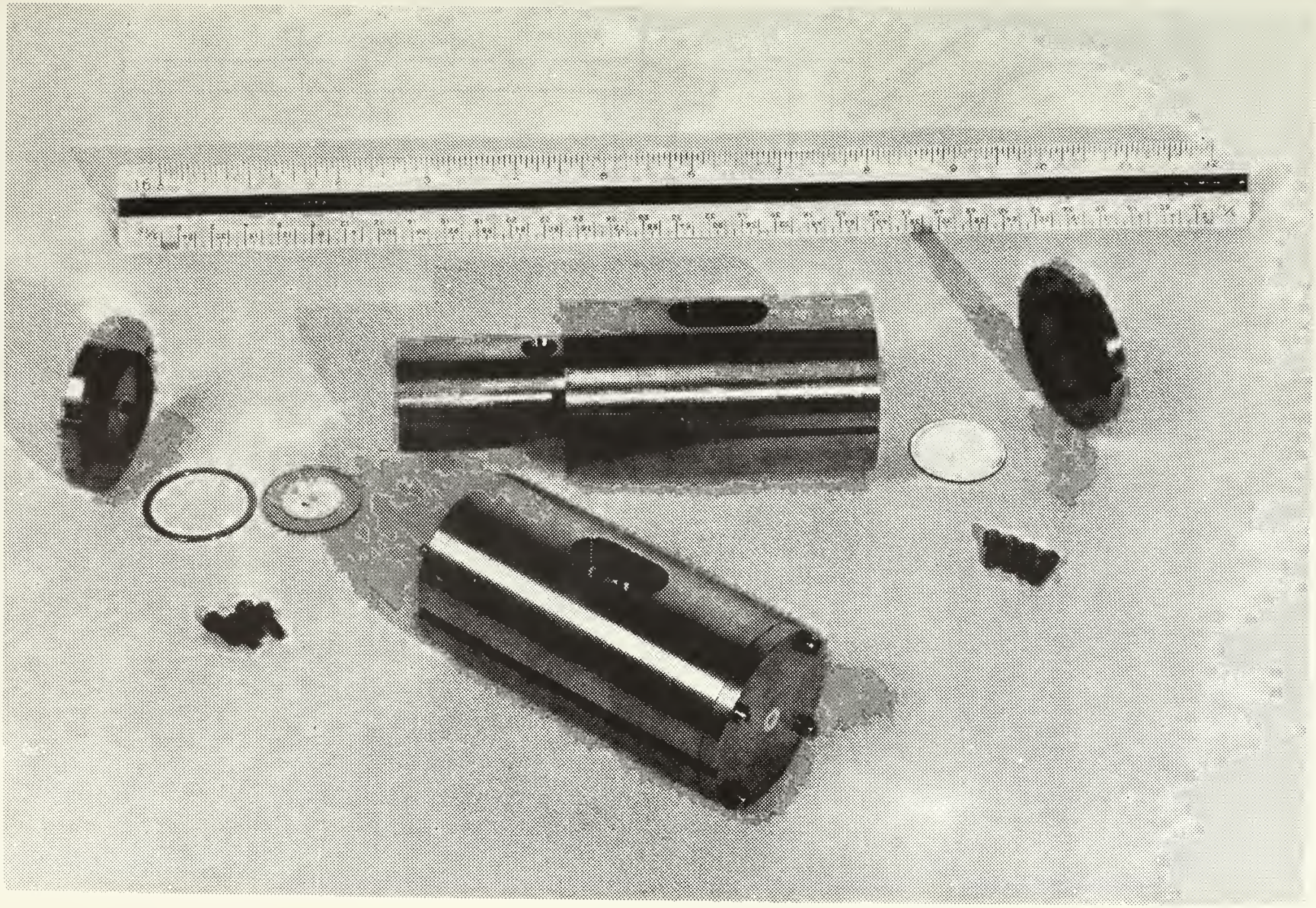


Figure 1. Outer Delay Line Jacket and Inner Sleeve.

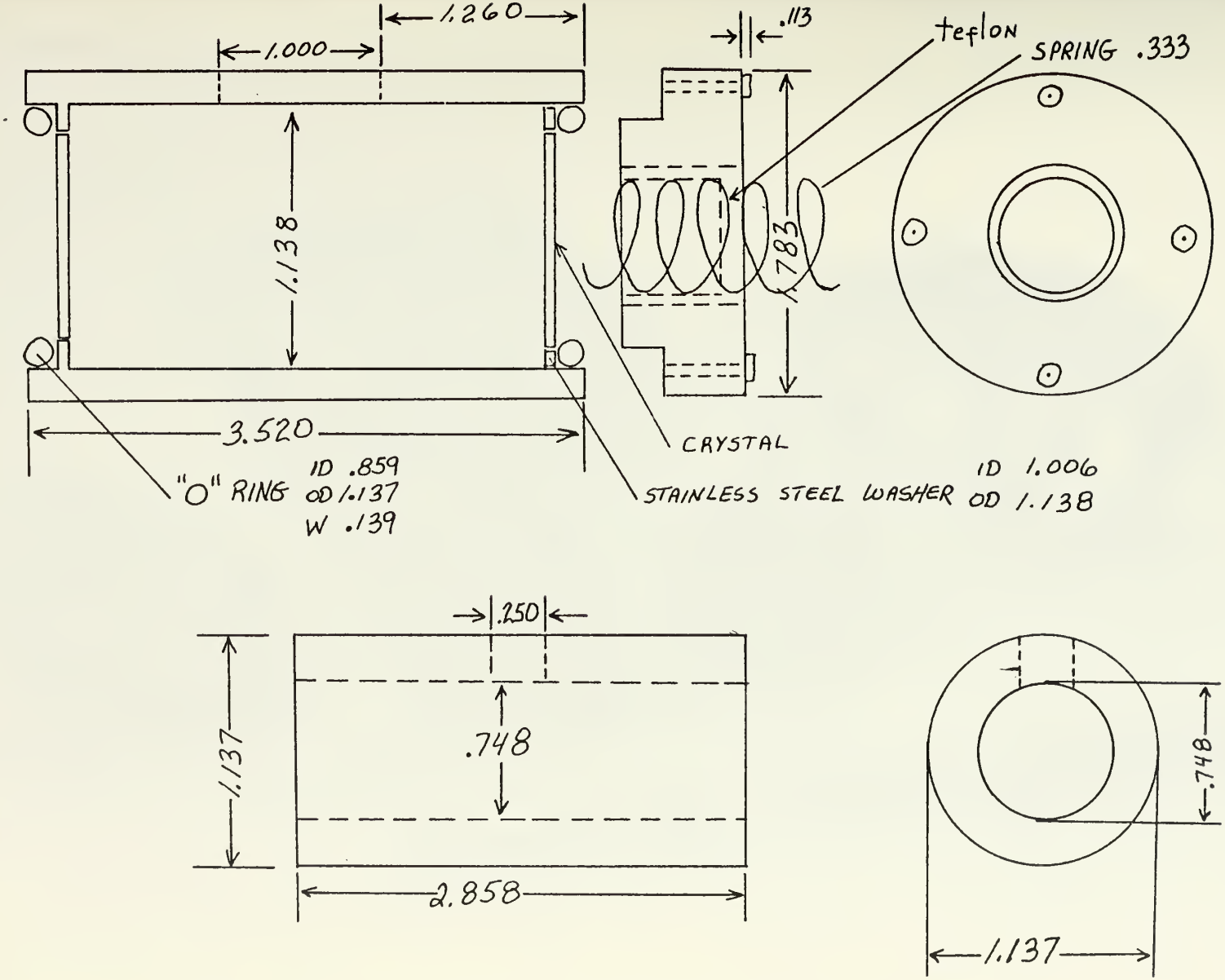


Figure 2. Outer Delay Line Jacket and Inner Sleeve

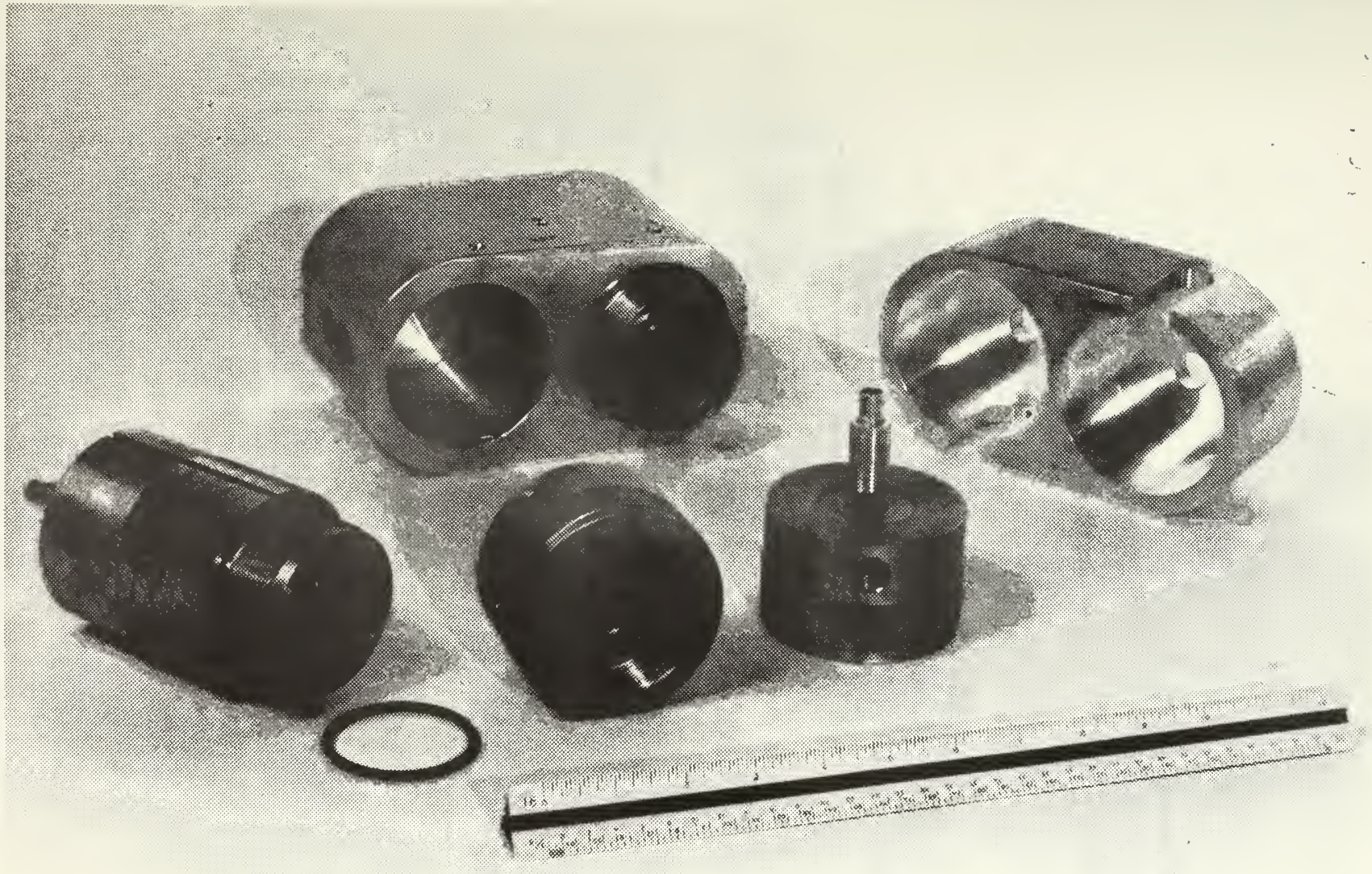


Figure 3. Pressure Vessels and Thermal Jacket

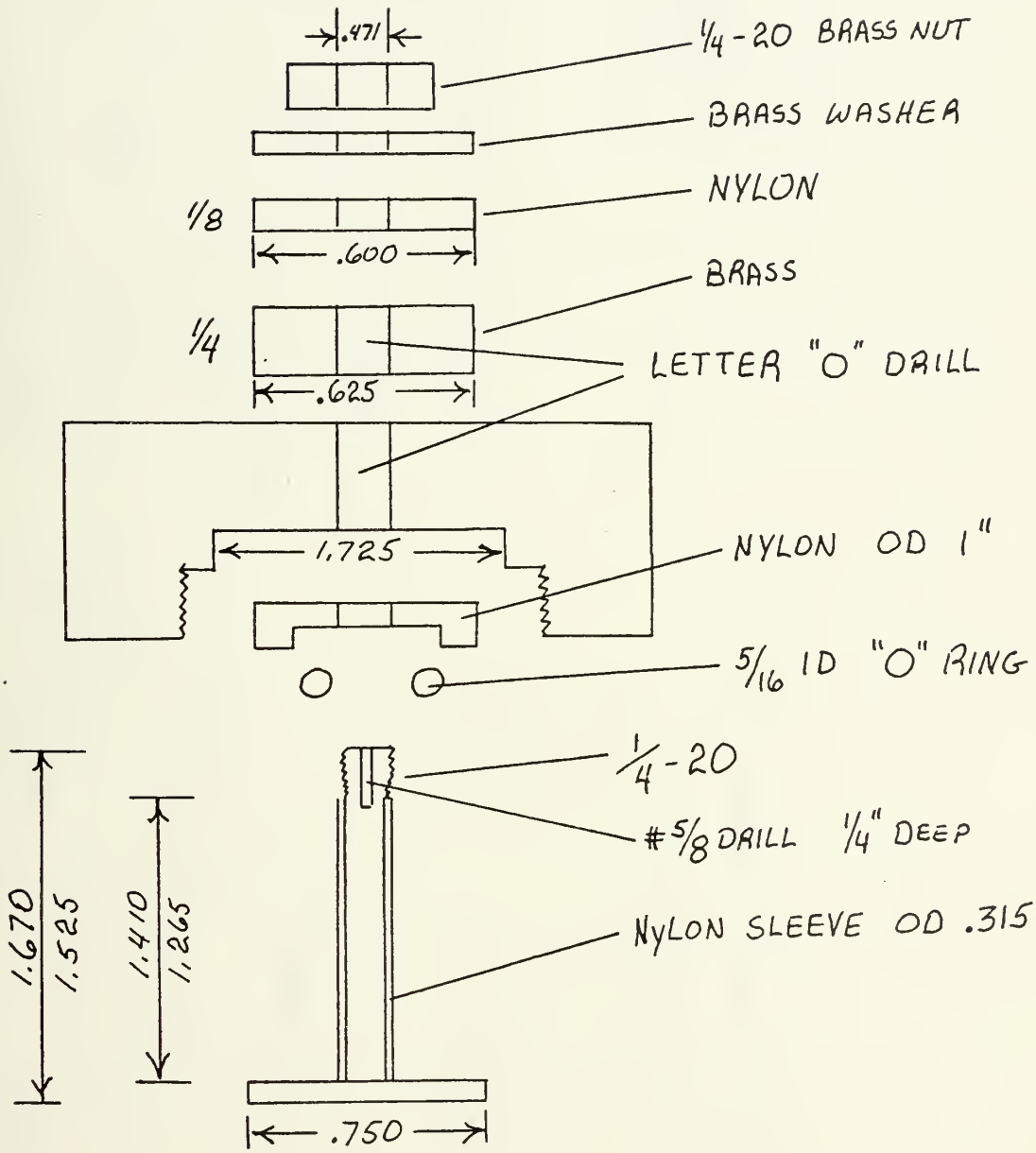


Figure 4. Diagram of Pressure Vessel Cap

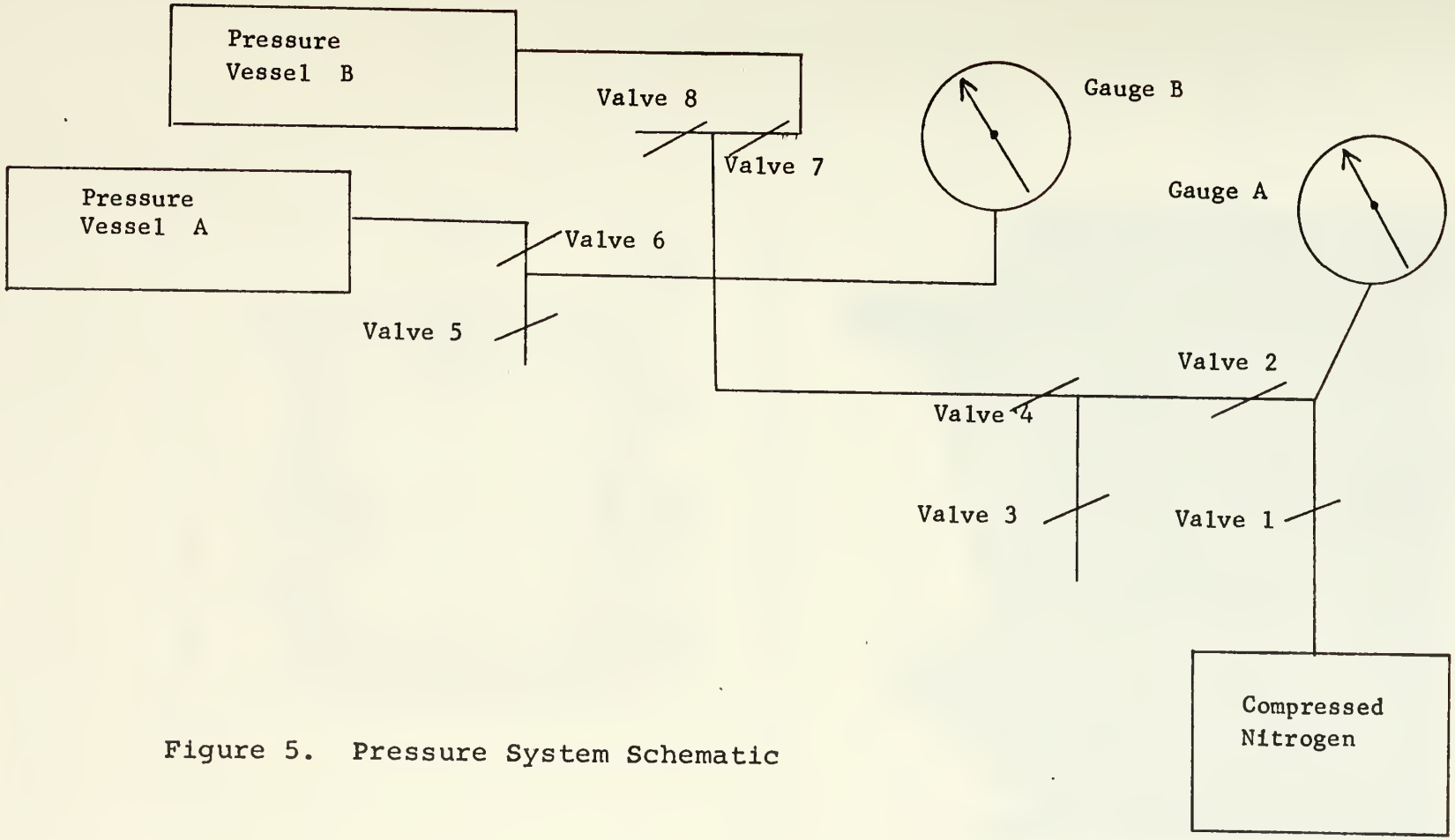
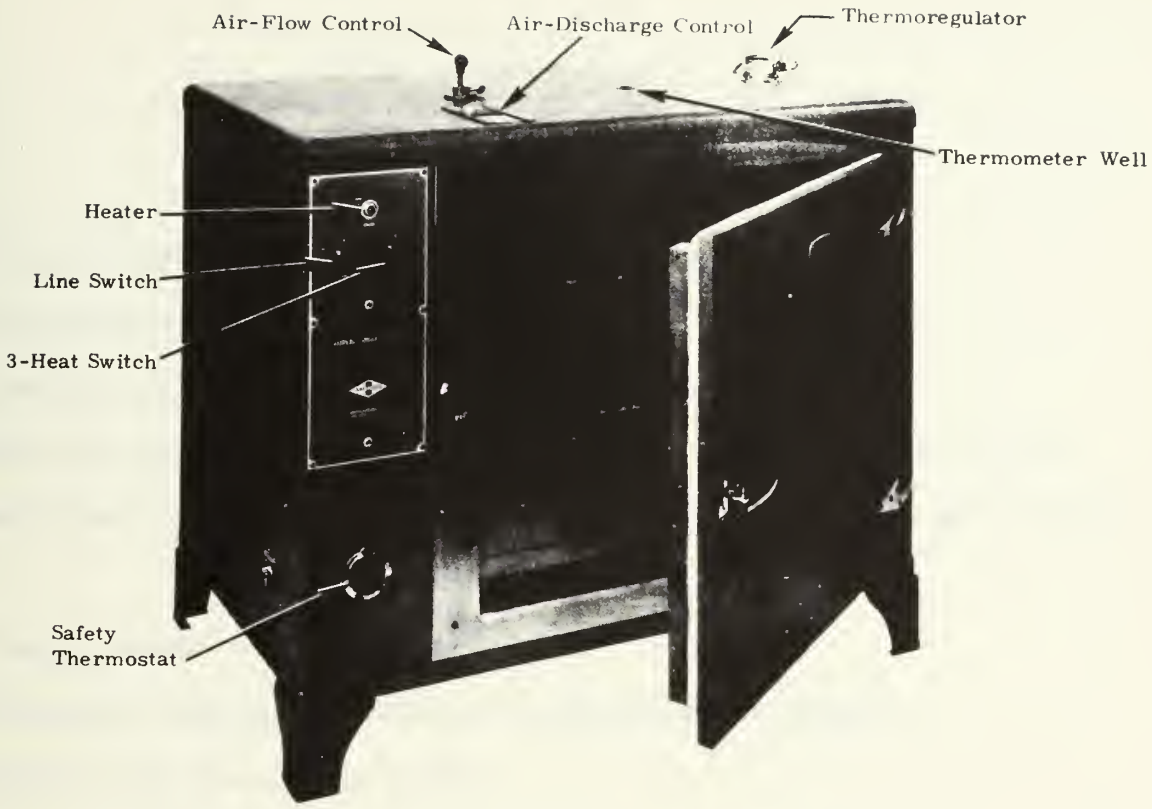
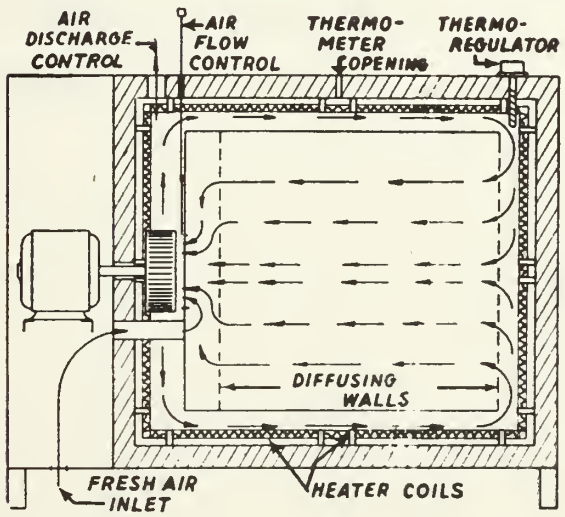


Figure 5. Pressure System Schematic



Aminco Forced-Convection Oven, Cat. No. 4-3540.



Typical Oven Cross-Section, Showing Air Flow

Figure 6. Temperature Control System

LIST OF EQUIPMENT

Oscillator: General Radio Company Type 1310-A

Electronic Counter: Hewlett-Packard 5233L

Thermistor Thermometer: Digitec Model 551-2

Unit Pulse Generator: General Radio Company Type 1217-B

Oscilloscope: Fairchild Type 777 Dual Beam with Dual Trace Plug-ins

Oven: Aminco Forced-Convection

Pressure Supply: Bottle of Compressed Nitrogen

Delay Line and Accessories

Pressure Vessels and Accessories

Thermal Jacket

Amplifier: Tektronix Type 1121

High Pass Filter

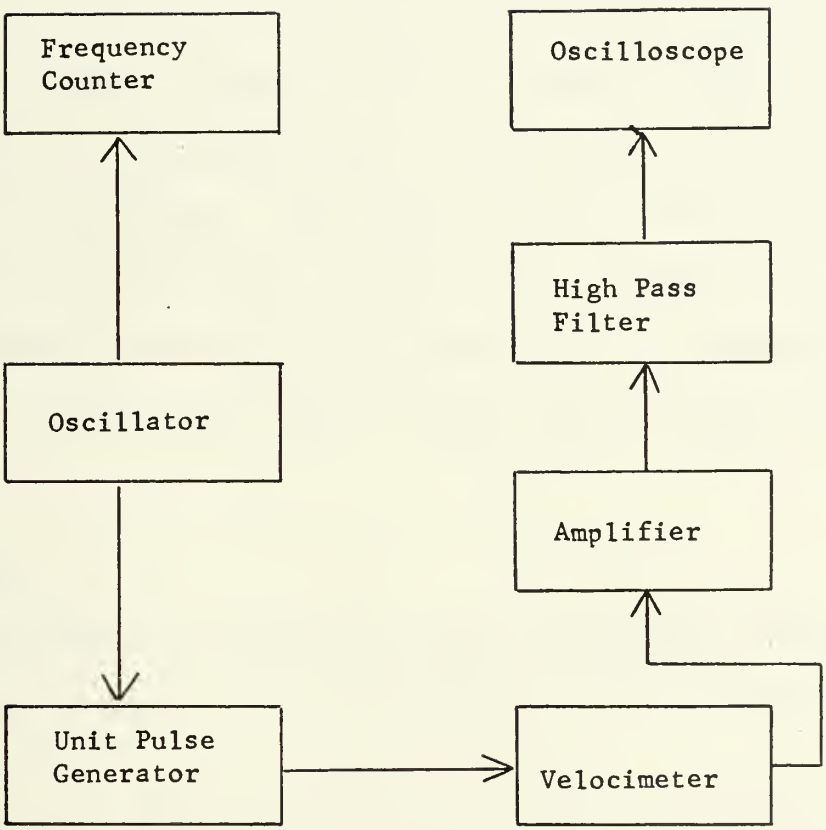


Figure 7. Block Diagram of Instrumentation

III. CLEANING, LOADING AND MEASURING PRODEDURES

A. CLEANING

Prior to every major run of the equipment all stainless steel parts of the delay line were first washed with a soap compound "Triam" to remove grease and dirt and were then chemically cleaned in a solution containing equal parts by volume of Acetone, Benzene, and 2-Propanol. The "O" rings were rinsed in distilled water and were then coated with a thin film of vaseline. The brass bar and the springs which furnished the electrical contacts were cleaned with a crocus cloth. Rubber gloves were then used in all subsequent handling of the delay lines to keep them as clean as possible.

B. LOADING

The assembly of the delay lines was always accomplished in the same manner to prevent damage to the crystals as follows:

The inner sleeve of the delay line was slipped through the • coded end of the outer delay line jacket very carefully insuring that the lip at the • end was not damaged. The stainless steel washer was then placed on the inner sleeve on the •• end. Next the 5 MHz transducer crystal was placed very carefully (the crystals were extremely fragile) inside the stainless steel washer with the fully plated side down toward the cavity of the inner sleeve. A

"O" ring was then placed on the •• coded end of the end plate and fastened in place using 4 allen head screws. The delay line was turned over and sealed in a similar manner except that the lip at the • end acts as the stainless steel washer. The "O" ring provided a liquid seal for the sample liquid in the delay line. The sample liquid was placed into the delay line through the bore in the top of the delay line and was filled half way to the top to allow for temperature variations. After the delay lines were loaded with the sample liquid they were placed into a bell shaped jar and subjected to a vacuum for approximately thirty minutes to remove air bubbles contained within the liquid. The delay lines were then placed into the pressure vessels, the thermal jacket was attached, and the pressure vessels were connected to the pressure system.

C. MEASURING

The system was allowed to reach equilibrium which generally meant that temperatures were set at the close of business on one day and the system allowed to reach equilibrium overnight. In some runs where the temperature was not changed but the pressures were cycled from 0 to 1500 psi in increments of 500 psi, it was determined through experimentation that equilibrium was reached in approximately 3 hours. Measurements were made by using the vernier control on the oscillator in conjunction with an oscilloscope and expanded horizontally to the maximum extent (0.05×10^{-6} sec). In

the early part of the experiment the vertical control of the oscilloscope was set to a convenient value (normally 1 volt/div). The vernier control of the oscillator was then used to obtain the maximum amplitude on the peak of the first half cycle insuring that the peak observed was in fact the superposition point. There was no difficulty in determining this peak as the vernier control could vary the frequency back and forth through the superposition peak and on the low frequency side the echoes would "leak through" and on the high frequency side the echoes would move off of the oscilloscope. This measuring technique left quite a bit to be desired and lead to precisions of about 0.6 Hz. In the latter part of the experiment a revised technique which amounted to utilizing the maximum vertical amplification (typically 0.1 volt/div) and positioning the first half cycle such that only the top of the superposition peak was observable. This technique vastly improved the precision of the data taken and lead to precisions of about 0.2 Hz.

IV. CALIBRATION

A. TEMPERATURE

To compare the superposition frequencies of two velocimeters located at two different positions in the oven, it was essential to determine the effect of temperature and pressure variations within the oven. The temperature calibration was conducted first. Both velocimeters A and B were loaded with distilled water and placed into the pressure vessels with the thermal jacket attached. The temperature was cycled from 35° to 70°C in increments of 5°C. At each temperature the system was allowed to reach equilibrium as mentioned earlier by setting the temperature on one day and making the readings on the next day. At each temperature the positions of the velocimeters were switched such that the pulse repetition frequencies were measured for both velocimeters in front and in back of the oven. Table I, columns 2 and 3 show the results of this calibration run. Column 4 was obtained using Equation (1). Recall that the minor modification mentioned in Section II. C., enabled the velocimeters to be interchanged in this experiment, thus readings were made for each velocimeter both in front and in back of the oven. Precise measurements were made by maximizing the amplitude of the superposition peak very carefully and determining the pulse repetition frequency from the electronic counter which measured the frequency of superposition to the nearest 0.1 Hz. Ten readings were made as each setting.

Recall from standard statistical theory that the estimate $\bar{x}$ of the quantity x, given x_i readings of the same quantity, is given by

$$\bar{x} = \frac{1}{n} \sum_{i=1}^{n} x_i$$

and the rms error is given by

$$x = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (x_i - \bar{x})^2}$$

that the estimate of x is $\bar{x} \pm x$.

The pulse repetition frequencies for velocimeters A and B are

f_{A_i} = the measured superposition frequency for velocimeter A

f_{B_i} = the measured superposition frequency for velocimeter B

then the ratio of lengths ℓ_A / ℓ_B is found from

$$c = 2\ell_A f_A$$

$$= 2\ell_B f_B$$

to be

$$\frac{\bar{f}_A \pm f_A}{\bar{f}_B \pm f_B} = \frac{\bar{f}_A}{\bar{f}_B} \left[1 \pm \sqrt{\left(\frac{f_A}{\bar{f}_A}\right)^2 + \left(\frac{f_B}{\bar{f}_B}\right)^2} \right] \qquad (1)$$

To determine the effect of the temperature variation on the pulse repetition frequency f_B/f_A within the oven,

assume velocimeter A is in front of the oven and velocimeter B is in back of the oven. Then for the same material (303 stainless steel) we have

$$\ell_A = \ell_{A_o} \left[1 + \quad (T_1 - T_0) \right] \tag{a}$$

$$\ell_B = \ell_{B_o} \left[1 + \quad (T_2 - T_0) \right] \tag{b}$$

where T_1 is the temperature in front and T_2 is the temperature in back of the oven. Dividing (a) by (b) and recognizing that $\alpha (T - T_0)$ is $\ll 1$, we then obtain

$$\frac{\ell_A}{\ell_B} = \frac{\ell_{A_o}}{\ell_{B_o}} \left[1 + \quad (T_1 - T_2) \right] \tag{c}$$

Similarly, for the same fluid in both velocimeters, we have

$$c_A = c_o \left[1 + \frac{1}{c_o} \frac{\partial c}{\partial T} (T_1 - T_o) \right] \tag{d}$$

and

$$c_B = c_o \left[1 + \frac{1}{c_o} \frac{\partial c}{\partial T} (T_2 - T_o) \right] \tag{e}$$

and obtain

$$\frac{c_B}{c_A} = 1 - \frac{1}{c_o} \frac{\partial c}{\partial T} (T_1 - T_2) \, . \tag{f}$$

From the general expression $c = 2\ell f$ we obtain

$$c_A = 2\ell_A f_A \tag{g}$$

$$c_B = 2\ell_B f_B \tag{h}$$

so that

$$\left(\frac{f_B}{f_A}\right)_{A \text{ in front}} = \frac{\ell_{A_o}}{\ell_{B_o}} \left[1 + \left(\alpha - \frac{1}{c_o}\frac{\partial c}{\partial T}\right) (T_1 - T_2) \right]. \quad \text{(i)}$$

Now, since an exchange of A and B in position in the oven with fixed temperature means that T_1 and T_2 are exchanged, then the above formula becomes

$$\left(\frac{f_B}{f_A}\right)_{B \text{ in front}} = \frac{A_o}{B_o} \left[1 - \left(\alpha - \frac{1}{c_o}\frac{\partial c}{\partial T}\right) (T_1 - T_2) \right]. \quad \text{(j)}$$

Then

$$\left(\frac{f_B}{f_A}\right)_{A \text{ in front}} - \left(\frac{f_B}{f_A}\right)_{B \text{ in front}} = 2\frac{\ell_{A_o}}{\ell_{B_o}} \left[\left(\alpha - \frac{1}{c_o}\frac{\partial c}{\partial T}\right) (T_1 - T_2) \right] \quad (2)$$

which provides a means of estimating $T_1 - T_2$.

Finally the true value of ℓ_{A_o}/ℓ_{B_o} is found by adding (i) and (j) and obtaining

$$\frac{\ell_{A_o}}{\ell_{B_o}} = \frac{1}{2} \left[\left(\frac{f_B}{f_A}\right)_{A \text{ in front}} + \left(\frac{f_B}{f_A}\right)_{B \text{ in front}} \right] \quad (3)$$

The values of ℓ_{A_o}/ℓ_{B_o} as a function of temperature are shown in Figure 8a for the data in Table 1. The data were fitted to a straight line obtaining

$$\frac{\ell_{A_o}}{\ell_{B_o}} = 1.000042 + (1.09 \times 10^{-7})\ (T - 35^{o}C)$$

From the scatter of each datum of $\pm$ 0.000019 resulting from the error in f_A and f_B, the estimated uncertainty in slope is about $\pm$ $1.09 \times 10^{-6}/^{o}C$ so that ℓ_{A_o}/ℓ_{B_o} can be taken as independent of temperature within our measurement error. The average value of ratios of lengths of the two velocimeters for the data in Table I and using (3) is

$$\overline{(\ell_{A_o}/\ell_{B_o})} = 1.000044 \pm 12$$

where the $\pm$ errors were calculated from the rms deviation of each value of the ratio from the average ratio. This value of $\overline{(\ell_{A_o}/\ell_{B_o})}$ is consistent with the value of $\overline{(\ell_{A_o}/\ell_{B_o})}$ = 1.000036 $\pm$ 7 obtained from the data on page 29 of Dawson's thesis, Run I, cycle 1 and 2, neglecting the data at $85^{o}C$ which were outside the temperature interval of interest in this experiment.

Values for ΔT were obtained from (2) which reduces to

$$\Delta T \approx \frac{c_o}{2} \frac{1}{\frac{\partial c}{\partial T}} \left[(f_B/f_A)_{A \text{ in front}} - (f_B/f_A)_{B \text{ in front}} \right]$$

since $\ell_{A_o}/\ell_{B_o} \approx 1$ and the value of $\frac{c_o}{\frac{\partial c}{\partial T}}$ is $>> \alpha$

where α is the thermal expansion coefficient and in the range 25° to 100°C for 303 stainless steel = 17.3 x 10^{-6}/°C[5]. Using c_o and $\partial c/\partial T$ the speed of sound and the change in speed of sound as a function of temperature from reference 6, the values of ΔT as a function of temperature were obtained and are shown in Figure 8b for the data in Table I. The average value of $\overline{\Delta T}$ for the two positions is $\overline{\Delta T}$ = 0.0113 ± 0.0149 °C where the ± errors were calculated from the rms deviation of each value of ΔT from the average value. This value is consistent with the value of $\overline{\Delta T}$ = 0.007 ± 0.006 °C obtained from the data on page 29 of Dawson's thesis, Run I, cycle 1 and 2, again neglecting the data at 85°C which were outside the temperature interval of interest in this experiment. The errors shown on Figure 8b were obtained from

$$\varepsilon_T = \frac{\varepsilon_f}{2} \frac{c_o}{\frac{\partial c}{\partial T}}$$

and increase sharply with temperature because of $\frac{\partial c}{\partial T}$ which decreases from a value of 2.00 m/sec-°C at 35°C to 0.19 m/sec - °C at 75°C, whereas ε_f (the error in f_A and f_B determined to be ± .000019 over the interval of temperature) and c_o (the speed of sound from reference 6) did not change appreciably over the temperature interval of 35° to 75°C.

TABLE I. Parameters from Temperature Calibration and Computations from Eq. (1)

TEMPERATURE (degrees C)	PULSE REPETITION FREQUENCY (KHz) f_A		f_B		RATIO f_B/f_A	
35.3	10.48531	± 12	10.48562	± 15	1.000030	± 18
35.3	10.48569	21	10.48603	28	32	34
40.1	10.54354	21	10.54409	18	52	26
40.1	10.54401	14	10.54475	32	70	33
44.9	10.59360	25	10.59365	26	13	34
44.9	10.58347	16	10.59409	18	58	23
50.3	10.63773	16	10.63831	12	54	18
50.4	10.63852	20	10.63916	29	60	34
55.3	10.66971	19	10.67001	08	28	20
55.2	10.66973	18	10.66947	32	24	30
60.6	10.69409	23	10.69457	18	45	28
60.6	10.69393	18	10.69447	20	50	26
66.0	10.70938	21	10.70983	27	42	33
66.0	10.70934	17	10.70991	20	60	25
71.1	10.71598	19	10.71645	11	44	20
71.3	10.71602	23	10.71651	13	45	24

Note: First entry at each temperature is for velocimeter A in front of oven and velocimeter B in back of oven and second entry is for positions reversed.

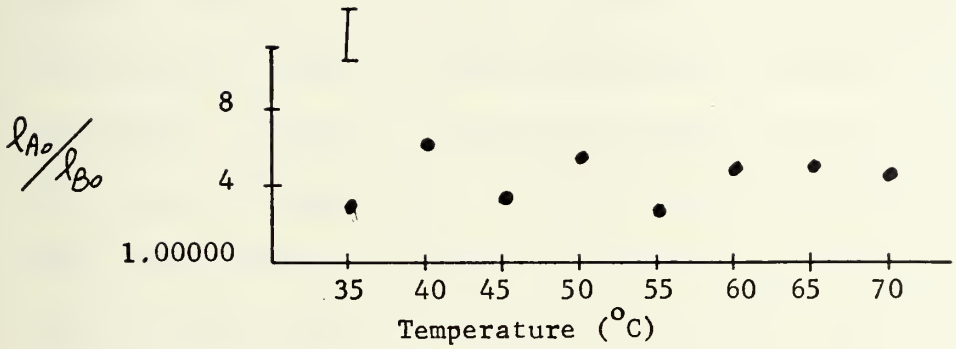


Figure 8a. Ratios of calculated length of velocimeter A to length of velocimeter B vs Temperature at Pressure of 0 psi.

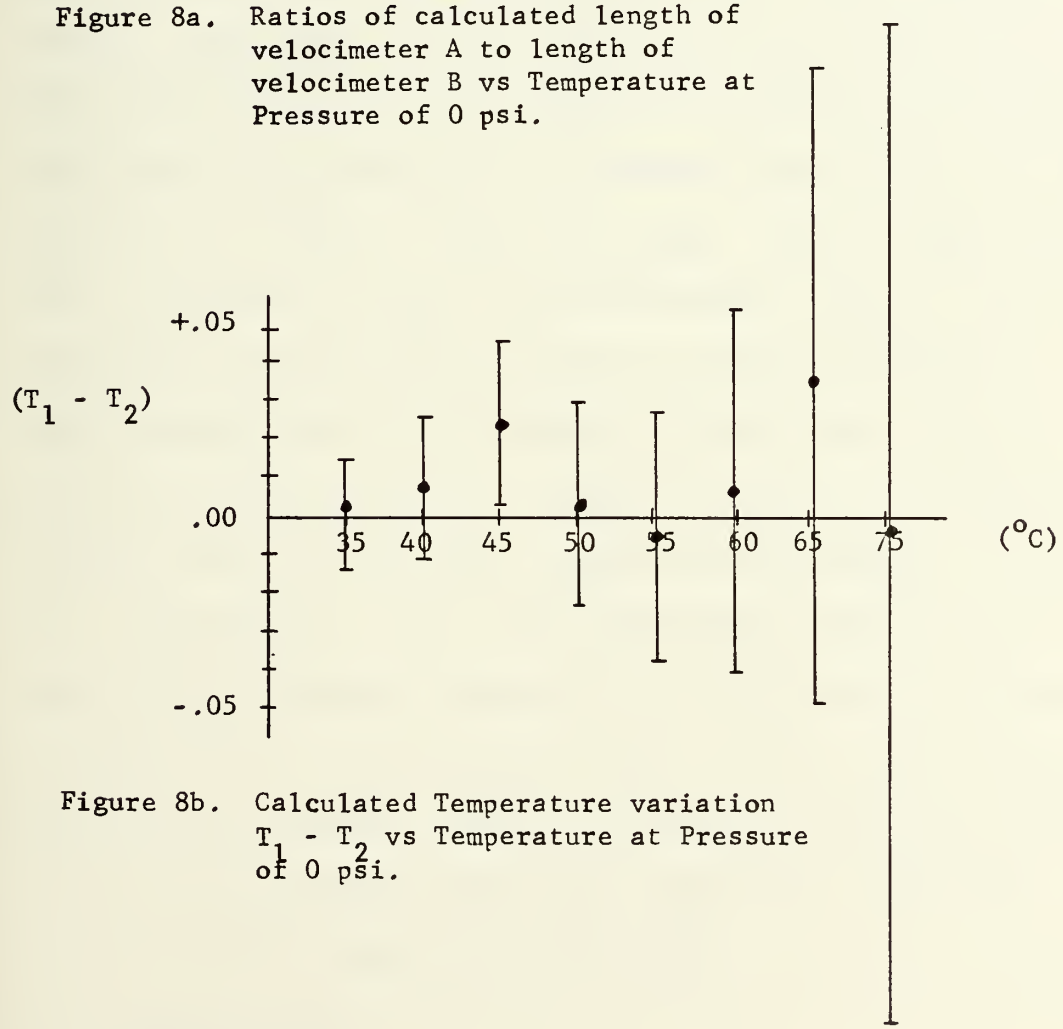


Figure 8b. Calculated Temperature variation $T_1 - T_2$ vs Temperature at Pressure of 0 psi.

B. PRESSURE

Pressure calibration was accomplished in a similar manner. Both velocimeters A and B were loaded with distilled water. Pressure was varied from 0 to 1500 psi in increments of 500 psi at each of three different temperature (35^{o}, 45^{o}, and 55^{o}C). Table II, columns 3 and 4 contain the results of this run. Column 5 was obtained using equation (1). The data are plotted in Figure 9 and the rms slopes are shown in solid (cycle up to 1500 psi) and dashed (cycle down to 0 psi) lines. The slopes varied from -2.4×10^{-9} to $+1 \times 10^{-9}$/psi. From the scatter of each datum of $\pm$ .000006 resulting from the eror in f_A and f_B, the estimated uncertainty in slope is about 8×10^{-9}/psi so that ℓ_{A_o}/ℓ_{B_o} can be taken as independent of pressure within our measurement error. With the exception of two points on the top graph of Figure 9, the three graphs show the stability of the ratio f_B/f_A as a function of the pressure. Neglecting these two points, the average ratio of the pulse repetition frequency of velocimeter B to velocimeter A over the temperature range of 35^{o} to 55^{o}C and over the pressure range of 0 to 1500 psi was found to be 1.000031 ± 10. This average value of the ratio of the pulse repetition frequency (f_B/f_A) was used in the NaCl run to correct for instances when the velocimeter contained a NaCl solution rather than distilled water.

C. SUMMARIZATION

Before concluding the calibration section it would be appropriate to summarize the salient points. In both the

temperature and pressure calibration the constancy of the ratios of lengths within the measurement error of the experiment was apparent. This experiment yielded a value of 1.000044 ± 12 for ℓ_{A_o}/ℓ_{B_o} whereas Dawson's experiment yielded a value of 1.000036 ± 7. The magnitude of temperature variations within the oven were calculated using Equation (2) and were found to be $0.0113 \pm 0.0149^{o}C$ for this experiment and $0.007 \pm 0.006^{o}C$ for Dawson's experiment. Dawson's values of ΔT were obtained by direct measurement and are more precise than values obtained by calculating differences in pulse repetition frequencies and using Equation (2) in this experiment but the values are consistent.

TABLE II. Parameters from Pressure Calibration and Computations from Eq. (1)

TEMPERATURE (degrees C)	PRESSURE (psi)	PULSE REPETITION FREQUENCY (KHz) f_A		f_B		RATIO f_B/f_A	
36.1	0	10.49590	± 24	10.49629	± 13	1.000037	± 26
36.0		10.49447	16	10.49489	20	40	25
36.1	500	10.53681	18	10.53710	17	28	24
36.1		10.53669	24	10.53787	31	112	38
36.1	1000	10.57697	23	10.57701	18	37	26
36.1		10.57825	19	10.57934	15	103	23
36.0	1500	10.61637	22	10.61669	16	30	26
46.4	0	10.60746	16	10.60767	24	20	28
46.5		10.60865	27	10.60888	21	22	32
46.5	500	10.65007	27	10.65060	18	50	30
46.5		10.64987	16	10.65023	26	34	28
46.5	1000	10.69292	24	10.69334	24	39	32
46.5		10.69264	15	10.69249	14	14	19
46.5	1500	10.73487	21	10.73499	20	11	27
56.0	0	10.67441	09	10.67457	21	15	21
56.0		10.67455	09	10.67569	07	13	11
55.9	500	10.71770	14	10.71828	14	54	19
56.0		10.71634	08	10.71681	06	44	10
55.9	1000	10.76046	07	10.76091	22	29	22
56.0		10.75963	19	10.76007	08	41	19
56.0	1500	10.80135	10	10.80162	10	25	13

Note: At each temperature the pressure was cycled from 0 psi to 1500 psi in increments of 500 psi. The first entry at each pressure is for data obtained cycling up to 1500 psi and the second entry is for data obtained cycling back down to 0 psi.

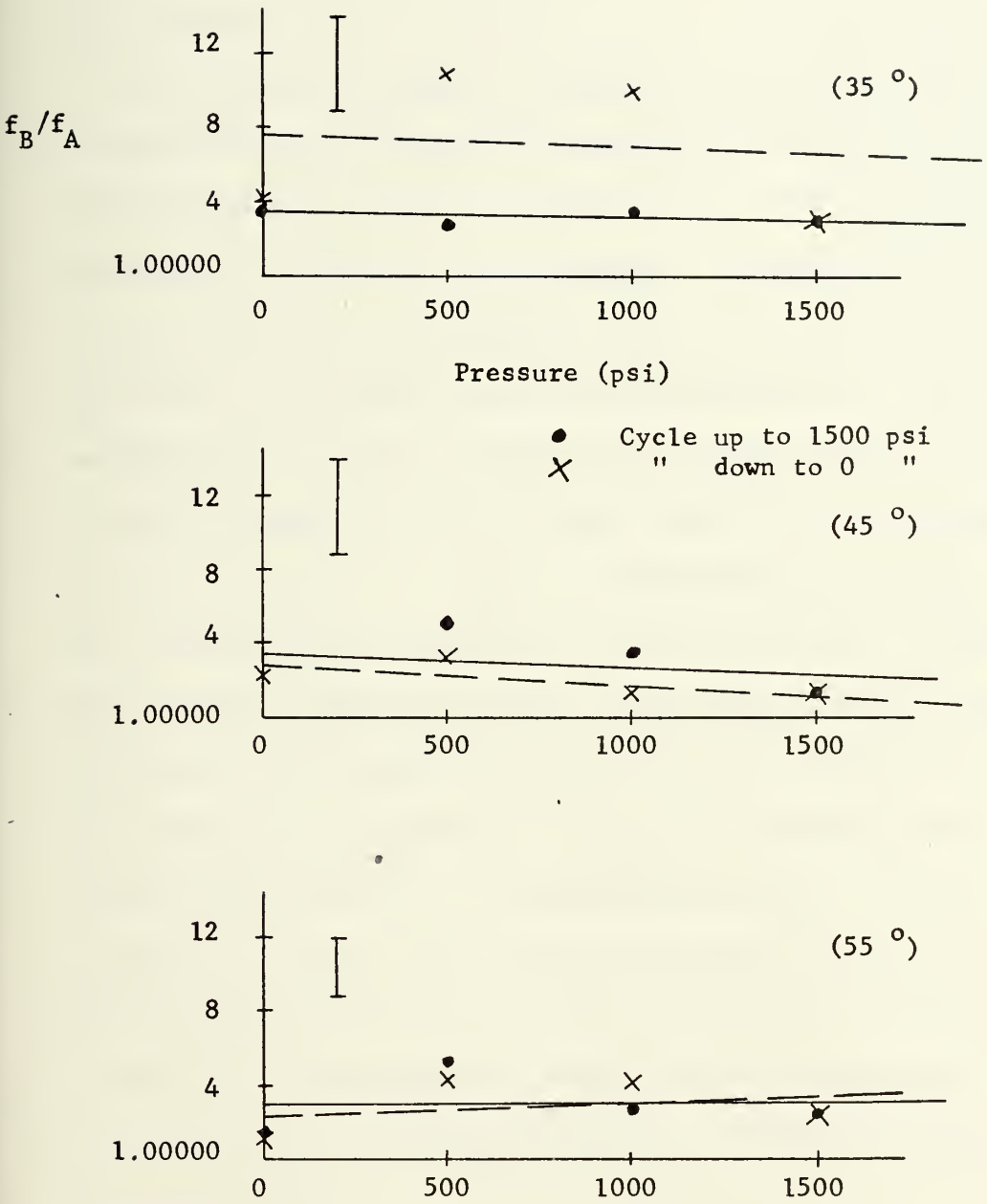


Figure 9. Ratios of Superposition Frequencies vs Pressure at Temperatures of 35 °, 45 °, and 55 °C.

V. NaCl Run

A. MIXING

To measure changes in sound velocity as a function of a concentration of aqueous electrolyte solution in the concentration range 2×10^{-1} to 4×10^{-4} moles/liter, a stock solution of 1000 ml was prepared. 50 ml of the stock solution provided the necessary quantity (approximate volume of the delay line) for the high concentration limit (2×10^{-1} moles/liter) and by diluting the stock solution using various sizes of pipets (100 ml, 10 ml, and 1 ml) solutions of 4×10^{-2}, 4×10^{-3}, and 4×10^{-4} moles/liter were obtained. The concentration range 2×10^{-1} to 4×10^{-4} moles/liter and NaCl as the compound used to make the aqueous electrolyte solution were selected because of the availability of data for comparison purposes.[4] Prior to weighing the NaCl on an analytical balance, an approximate amount of the NaCl required (15 gms) was dried for several days at 100°C in the Aminco Oven and then cooled to room temperature in a Fisher Scientific Desicooler to remove excess moisture. Using the dried NaCl and a weighing bottle, 11.6886 $\pm$ .00005 gm were obtained since

$$x = \frac{2 \times 10^{-1} \text{ moles/liter}}{1 \text{ mole}/58.443 \text{ gm}} = 11.6886 \text{ gm/liter}$$

where x = the number of gm/liter required to form the stock solution concentration of 2×10^{-1} moles/liter. A 1000 ml

flask was used to mix the NaCl with distilled water by first filling the flask approximately half way and then adding the NaCl to the flask through a funnel. The 1000 ml flask was then brought to the correct level by rinsing the weighing bottle several times and pouring additional distilled water through the funnel thus insuring that negligible NaCl particles were left behind clinging to the weighing bottle or funnel. The final leveling of the 1000 ml flask was accomplished using an eye dropper adding a drop of distilled water at a time until the 1000 ml flask was judged to be exactly full.

The stock solution containing 2×10^{-1} moles/liter was then used to obtain lower concentrations by successive dilution: for example 4×10^{-2} moles/liter was obtained by filling a 500 ml flask approximately half way with distilled water and then adding 100 ml of the stock solution using 100 ml pipet since

$$2 \times 10^{-1} \text{ moles/liter} \times \frac{100 \text{ ml}}{500 \text{ ml}} = 4 \times 10^{-2} \text{ moles/liter.}$$

The 500 ml flask was then brought to the correct level by rinsing the pipet several times and then adding additional distilled water again using an eye dropper in the final stages of leveling. Similarly, concentrations of 4×10^{-3} and 4×10^{-4} moles/liter were obtained by using 10 ml and 1 ml pipets respectively.

B. DATA

The data obtained in the NaCl run for each of the four concentrations examined are presented in Tables III - VI. Velocimeter A was loaded with the NaCl solution in concentrations of 2×10^{-1} and 4×10^{-3} moles/liter (Tables III and V) and Velocimeter B was loaded with the NaCl solution in concentrations of 4×10^{-2} and 4×10^{-4} moles/liter (Tables IV and VI). In each instance the temperatures were set to nominal values of 35^{o}, 45^{o}, and 55^{o}C and the pressure was then varied from 0 psi to 1500 psi in increments of 500 psi. Columns 3 and 4 were obtained by averaging ten readings at each temperature and pressure setting after allowing approximately three hours for equilibrium conditions to be reached. Column 5 was obtained by taking the ratio of the higher pulse repetition frequency to the lower pulse repetition frequency and column 6 was obtained by relating the pulse repetition rate of the velocimeter loaded with the NaCl solution to the same velocimeter containing distilled water by using an average pulse repetition frequency f_B/f_A of 1.000031 obtained during the Pressure Calibration Run. Thus f_A'/f_A was obtained by using

$$f_A'/f_A = f_A'/f_B \times f_B/f_A = f_A'/f_B \times 1.000031$$

and similarly f_B'/f_B was obtained using

$$f_B'/f_B = f_B'/f_A \times \frac{1}{f_B/f_A} = f_B'/f_A \times .999969$$

where f' denoted the pulse repetition frequency with the NaCl solution.

TABLE III. Parameters from NaCl (2 X 10^{-1} moles/liter) Run and Computations from Eq. (1)

TEMPERATURE (degrees C)	PRESSURE (psi)	PULSE REPETITION FREQUENCY (KHz) f'_A	f_B	RATIO f'_A/f_B	RATIO f'_A/f_A
35.3	0	10.56739 ± 09	10.48541 ± 13	1.007818 ± 15	1.0078488 ± 19
35.4	500	10.60902 12	10.52655 08	7834 14	7865 19
35.3	1000	10.64909 12	10.56707 12	7762 16	7793 20
35.4	1500	10.68971 07	10.61810 06	6744 09	6775 16
46.7	0	10.68662 08	10.60011 07	8161 11	8192 17
46.7	500	10.72956 10	10.65290 09	7196 13	7227 18
46.8	1000	10.77112 09	10.69462 09	7153 12	7154 18
46.8	1500	10.81250 09	10.73641 09	7087 12	7118 18
56.6	0	10.75060 11	10.67747 09	6849 13	6880 18
56.6	500	10.79437 08	10.72128 08	6817 11	6848 17
56.6	1000	10.83709 12	10.76407 15	6784 18	6815 21
56.6	1500	10.87970 08	10.80680 08	6746 11	6777 17

Note: Velocimeter A loaded with NaCl and velocimeter B loaded with distilled water.

TABLE IV. Parameters from NaCl (4×10^{-2} moles/liter) Run and Computations from Eq. (1)

TEMPERATURE (degrees C)	PRESSURE (psi)	PULSE REPETITION FREQUENCY (KHz) f_A		f'_B		RATIO f'_B/f_A		RATIO f'_B/f_B	
36.4	0	10.49928	± 14	10.51634	± 13	1.001625	± 18	1.001594	± 21
36.4	500	10.54103	11	10.55691	10	1506	14	1475	19
36.4	1000	10.58225	12	10.59771	13	1461	16	1430	20
36.4	1500	10.62305	10	10.63835	12	1440	14	1409	19
45.4	0	10.59987	11	10.61428	14	1359	17	1328	20
45.4	500	10.64116	07	10.65608	14	1402	15	1371	19
45.4	1000	10.68371	10	10.69818	09	1351	13	1320	18
45.4	1500	10.72575	11	10.73989	08	1318	12	1287	18
56.5	0	10.67752	10	10.69178	12	1336	15	1305	19
56.6	500	10.72114	15	10.73555	09	1344	16	1313	20
56.6	1000	10.76450	11	10.77856	10	1306	13	1275	18
56.6	1500	10.80695	11	10.82165	09	1360	13	1329	18

Note: Velocimeter A loaded with distilled water and velocimeter B loaded with NaCl.

TABLE V. Parameters from NaCl (4 X 10^{-3} moles/liter) Run and Computations from Eq. (1)

TEMPERATURE (degrees C)	PRESSURE (psi)	PULSE REPETITION FREQUENCY (KHz) f'_A	f_B	RATIO f'_A/f_B	RATIO f'_A/f_A
34.9	0	10.48118 ± 12	10.48000 ± 12	1.000113 ± 16	1.000144 ± 20
34.9	500	10.52265 13	10.52078 12	178 17	209 20
34.9	1000	10.56370 08	10.56168 10	191 12	222 18
34.9	1500	10.60407 05	10.60189 07	205 08	236 15
45.8	0	10.60362 08	10.60247 08	108 11	139 17
45.8	500	10.64628 08	10.64445 11	173 13	204 18
45.8	1000	10.68821 10	10.68621 07	187 12	218 18
45.8	1500	10.72945 09	10.72753 07	179 10	210 16
55.9	0	10.67484 08	10.67371 07	106 10	137 16
55.9	500	10.71705 10	10.71902 10	184 13	215 18
55.9	1000	10.76311 07	10.76092 09	203 11	234 17
55.9	1500	10.80588 10	10.80363 07	208 12	239 18

Note: Velocimeter loaded with NaCl and velocimeter B loaded with distilled water.

TABLE VI. Parameters from NaCl (4×10^{-4} moles/liter) Run and Computations from Eq. (1)

TEMPERATURE (degrees C)	PRESSURE (psi)	PULSE REPETITION FREQUENCY (KHz) f_A	f'_B	RATIO f'_B/f_A	RATIO f'_B/f_B
35.8	0	10.49222 ± 09	10.49287 ± 08	1.000062 ± 12	1.000031 ± 16
35.7	500	10.53217 07	10.53279 07	59 09	28 15
35.8	1000	10.57272 06	10.57375 08	97 10	66 15
35.8	1500	10.61412 06	10.61517 08	99 10	68 15
44.9	0	10.59400 08	10.59459 09	56 11	25 16
44.8	500	10.63561 12	10.63633 07	68 13	37 17
44.8	1000	10.67685 08	10.67751 08	62 12	31 16
44.9	1500	10.71913 11	10.71961 07	45 12	14 16
55.5	0	10.67146 08	10.67201 09	52 11	21 16
55.5	500	10.71490 08	10.71553 08	59 11	28 16
55.5	1000	10.75843 08	10.75905 08	58 11	27 16
55.5	1500	10.80051 07	10.80117 07	61 11	30 16

Note: Velocimeter A loaded with distilled water and velocimeter B loaded with NaCl

VI. DATA EVALUATION AND CONCLUSIONS

A. DATA EVALUATION

The data obtained in the NaCl run were analyzed in two ways. First the available data for distilled water obtained at 0 psi and in the vicinity of 35°C along with data from the temperature and pressure calibration runs at 0 psi and 35°C were compared with data available from Greenspan and Tschiegg[6] on the speed of sound in distilled water as a function of temperature. Secondly the data from the NaCl run were compared with data from Garnsey, Boe, Mahoney, and Litovitz[4] on the change in the speed of sound as a function of the concentration of the electrolyte aqueous solution.

Table VII shows the available data for distilled water at 0 psi in the vicinity of 35°C. The first two entries for each velocimeter are from the temperature calibration (Table I), the third and fourth entries are from the pressure calibration (Table II), and the last two entries are from the NaCl run (Tables III - VI). The pulse repetition frequencies in velocimeter A were corrected using the averaged pulse repetition frequency ratio of 1.000031 from the pressure calibration run. The data are plotted in Figure 10 and show the dependence of the pulse repetition frequency on temperature. To compare the change of the speed of sound as a function of the temperature with data from Greenspan and Tschiegg[6] it was necessary to consider two regions of the data on Figure 10, since the dependence of the pulse

repetition frequency is not exactly linear with the temperature. The explanation for this discrepancy is not known but perhaps related to the temperature measuring thermistor thermometer variations within this temperature interval. Greenspan and Tschiegg recorded 1.94 m/sec-^{o}C at a temperature of 35.8^{o}C which is approximately the mid-point of the data on Figure 10. Using

$$\ell (T) = \ell_o (1 + \alpha T)$$

then

$$\frac{\Delta \ell}{\Delta T} = \ell_o \alpha \qquad \text{or} \quad \alpha = \frac{1}{\ell_o} \frac{\Delta \ell}{\Delta T} \tag{a}$$

and using $c = 2 \ell f$ (b)

obtain

$$\frac{\Delta c}{\Delta T} = 2\ell \frac{\Delta f}{\Delta T} + 2 f \frac{\Delta \ell}{\Delta T}$$

dividing by (b) and using (a) obtain

$$\frac{\Delta c}{\Delta T} = \frac{c}{f} \left(\frac{\Delta f}{\Delta T} + \alpha \right) \tag{4}$$

$\frac{\Delta f}{\Delta T}$ and f were obtained from the upper and lower portions of the curve on Figure 10, and c was obtained from the Tables of the Speed of Sound in Water from Reference 6.

TABLE VII. Pulse Repetition Frequency at 0 psi in the Vicinity of 35°C from Tables I - VI.

TEMPERATURE (degrees C)	PULSE REPETITION FREQUENCY (KHz)		SOURCE OF DATA (Table)
	f'_A	f_B	
35.3	10.48563	10.48562	I
35.3	10.48601	10.48603	I
36.1	10.49622	10.49629	II
36.0	10.49479	10.49489	II
35.3	-	10.48541	III
36.4	10.49960	-	IV
34.9	-	10.48000	V
35.8	10.49254	-	VI

Note: Pulse repetition frequency of Velocimeter A (f'_A) corrected using the averaged pulse repetition frequency ratio of 1.000031. Thus $f'_A = f_A \times 1.000031$

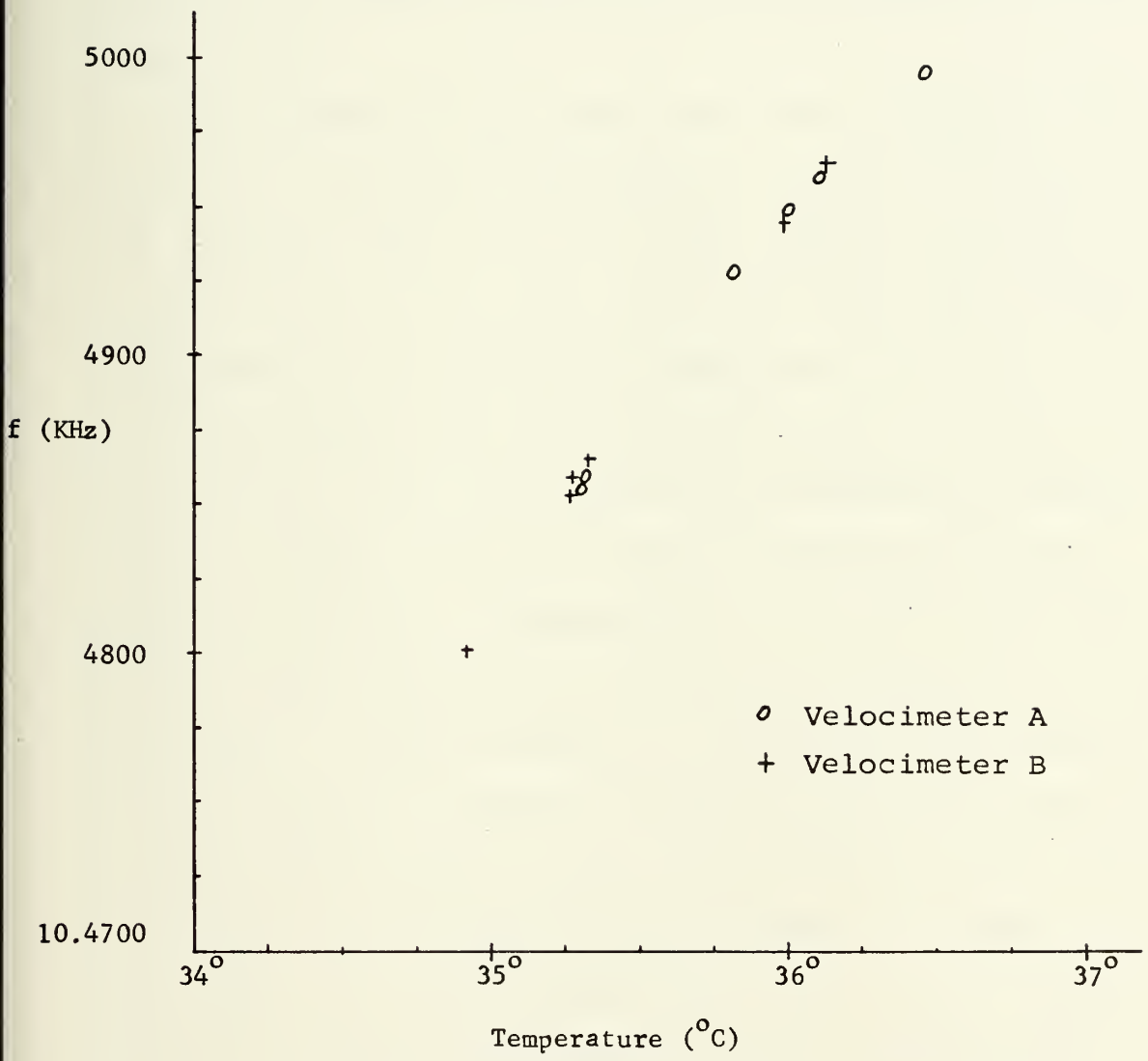


Figure 10. Pulse Repetition Frequency vs Temperature at 0 psi.

T(°C)	$\partial c/\partial T$ (m/sec-°C)	
	Greenspan	This work
35.5	1.97	2.02
36.25	1.92	1.70

Agreement is good but there is some discrepancy at the higher temperature.

An analysis of the pulse repetition frequency ratios (f'/f) for all four concentrations (column 6 of Tables III - VI) indicated that for some reason (perhaps excessive amounts of dissolved air at 0 psi) the pulse repetition frequencies determined at 0 psi for all temperatures were not consistent with the pulse repetition frequencies obtained at 500, 1000, and 1500 psi. The pulse repetition frequencies obtained at these pressures (with one notable exception at 35.4°C, 1500 psi, and at a concentration of 2×10^{-1} moles/liter) were of approximately the same magnitude and did not exhibit any trend to either increase or decrease as the pressure was varied from 500 to 1500 psi, whereas the pulse repetition frequencies obtained at 0 psi were in almost every instance at a very large variance from the mean of the data. For this reason the data obtained at 0 psi were not utilized in forming averages of the pulse repetition frequencies over the pressure range of 0 to 1500 psi. Disregarding the data at 0 psi and the one inconsistent reading at 35.4°C, 1500 psi and a concentration of 2×10^{-1} moles/liter, the remaining data were averaged over the pressure range of 500 to 1500 psi and the resulting averages are shown in column 3 of Table

VIII. These averages over the pressure interval were then averaged over the temperature interval and the results are shown in column 4 of Table VIII. The change in the speed of sound as a function of the concentration was calculated using

$$\Delta c = (1 - \bar{f}'/\bar{f})\, c$$

where

$\Delta c = c' - c$

c' = speed of sound in NaCl solution

c = speed of sound in distilled water

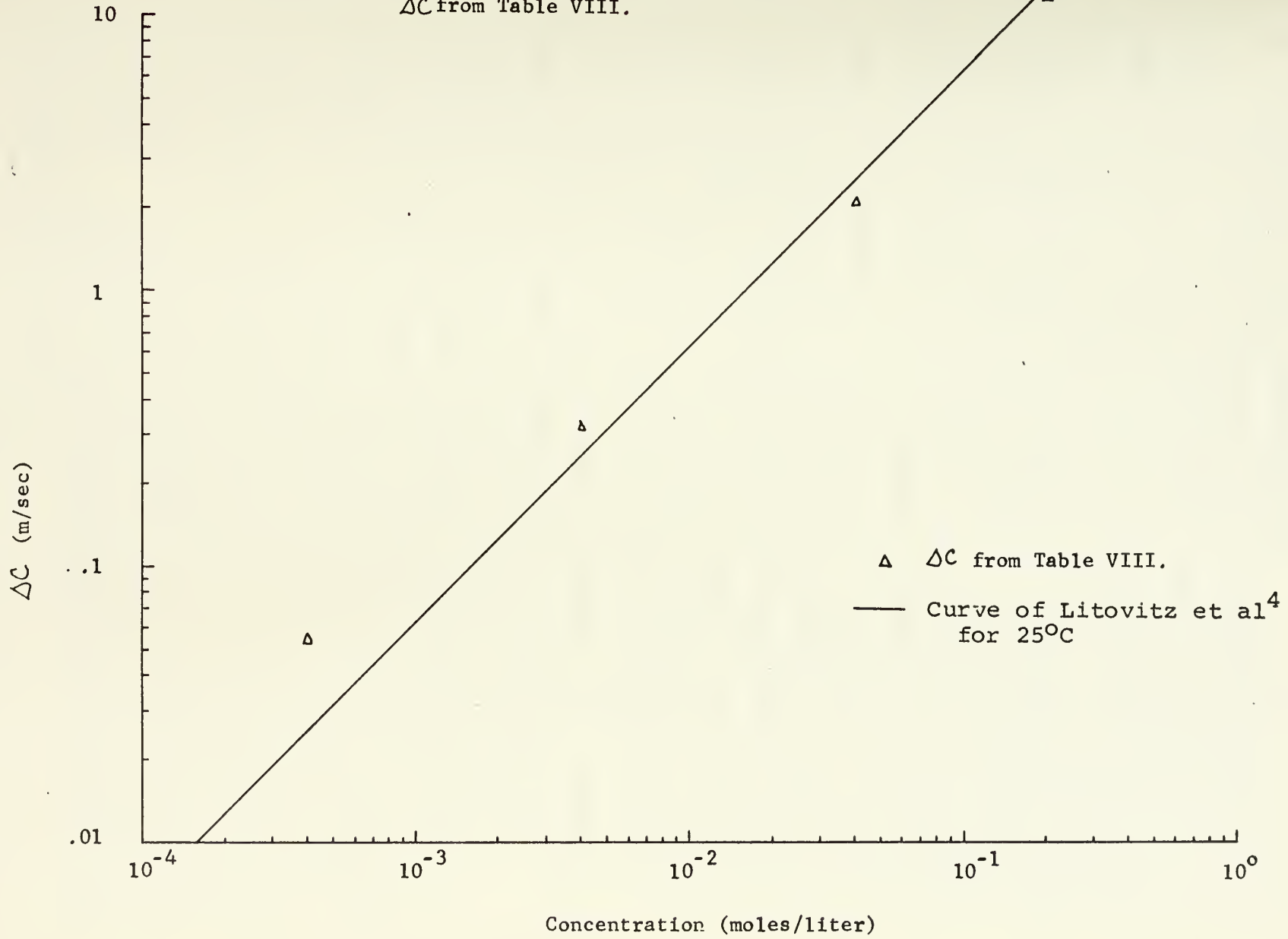
and $c = 1536.72$ m/sec, at a temperature of 45°C, from Tables of speed of sound in distilled water.[6] The change in speed of sound as a function of concentration is shown in column 5 of Table VIII and is plotted on Figure 11. This figure also shows the curve of the results at 25°C for the experiments of Garnsey et al[4]; the slope of their line is 66.0 (m/sec)/(mole/liter) in comparison with our result of 55.0 (m/sec)/(mole/liter) at 45°C. Figure 11 shows very close agreement between the change in the speed of sound as a function of the concentration from Reference 4 and the results of this experiment. The precision of the measurements in this experiment were limited mainly by variations in the equilibrium conditions for both temperature and pressure, varying quantities of dissolved air, evaporation and impurities. There may be a temperature effect in the difference of slopes, but resolution of this possibility depends upon further experimental study.

TABLE VIII. Reduction of Data from Tables III to VI

CONCENTRATION (moles/liter)	TEMPERATURE (degrees C)	AVERAGE (Over P)	AVERAGE (Over T)	Δc (m/sec)
2×10^{-1}	35	1.007829		
	45	7166	1.007269	11.17
	55	6813		
4×10^{-2}	35	1.001438		
	45	1326	1.001356	2.08
	55	1305		
4×10^{-3}	35	1.000222		
	45	210	1.000220	.338
	55	229		
4×10^{-4}	35	1.000054		
	45	27	1.000036	.055
	55	28		

Note: Δc obtained from $\Delta c = (1 - \text{Ave})\ 1536.72$ where 1536.72 is the speed of sound, at $T = 45^{\circ}C$, from tables of the speed of sound in water.[6]

Figure 11. ΔC vs Concentration at 45 °C and ΔC from Table VIII.



B. CONCLUSIONS AND RECOMMENDATIONS

A very precise velocimeter has been developed and utilized to measure changes in the speed of sound as a function of the concentration of an aqueous NaCl solution in the concentration range of 2×10^{-1} to 4×10^{-4} moles/liter. Using 2 velocimeters, one filled with distilled water and one filled with an aqueous NaCl solution, rigid temperature and pressure control, and averaging computations it was possible to obtain accurate speed of sound differences by measuring the pulse repetition frequencies which maximized the amplitude of the superposition peak on the oscilloscope. Temperature and pressure calibrations of the two velocimeters indicated the constancy of the ratio of the lengths of the two velocimeters and indicated the magnitude of temperature variations within the oven to be consistent with the value of 0.007 ± 0.006 obtained in prior research by Dawson. The averaging of the pulse repetition frequencies over the pressure and temperatures intervals could be improved by reducing the temperature and pressure increments and taking more data. A suggestion would be pressure increments of 200 psi over the pressure interval of 0 to 1500 psi and temperature increments of $5^{o}C$ over the temperature interval of 35^{o} to $55^{o}C$. The change in the speed of sound as a function of the concentration of aqueous electrolyte solutions was obtained and determined to be in very close agreement with available data from Litovitz.[4] Experimental results indicated that the speed of sound as a function of the concentration can be measured with a precision of ± 3 cm/sec.

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13. ABSTRACT

A very precise velocimeter has been developed and utilized to measure changes in the speed of sound as a function of the concentration of aqueous electrolyte solutions. The experimental results indicated that the speed of sound can be measured with a precision of $\pm$ 3 cm/sec. Using 2 velocimeters for comparison, one filled with distilled water and one filled with dilute aqueous solutions of NaCl, four separate runs were conducted at concentrations of 2×10^{-1}, 4×10^{-2}, 4×10^{-3}, and 4×10^{-4} moles/liter. The ratios of superposition frequencies vs. pressure, over the pressure range of 0 to 1500 psi in increments of 500 psi, and temperature, over the temperature range of 35° to 55°C in increments of 10°C, were obtained. The change in the speed of sound as a function of the concentration of NaCl in the concentration range 2×10^{-1} to 4×10^{-4} moles/liter is in agreement with data from Garnsey, Boe, Mahoney, and Litovitz from the Journal of Chemical Physics, v. 50, n. 12, pp. 5222-5228, 15 June 1969. The slope of the line at 45°C is 56.0 (m/sec)/(mole/liter) in reasonable agreement with the slope of 66.0(m/sec)/(mole/liter) from Litovitz et al for 25°C.

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Raymond

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